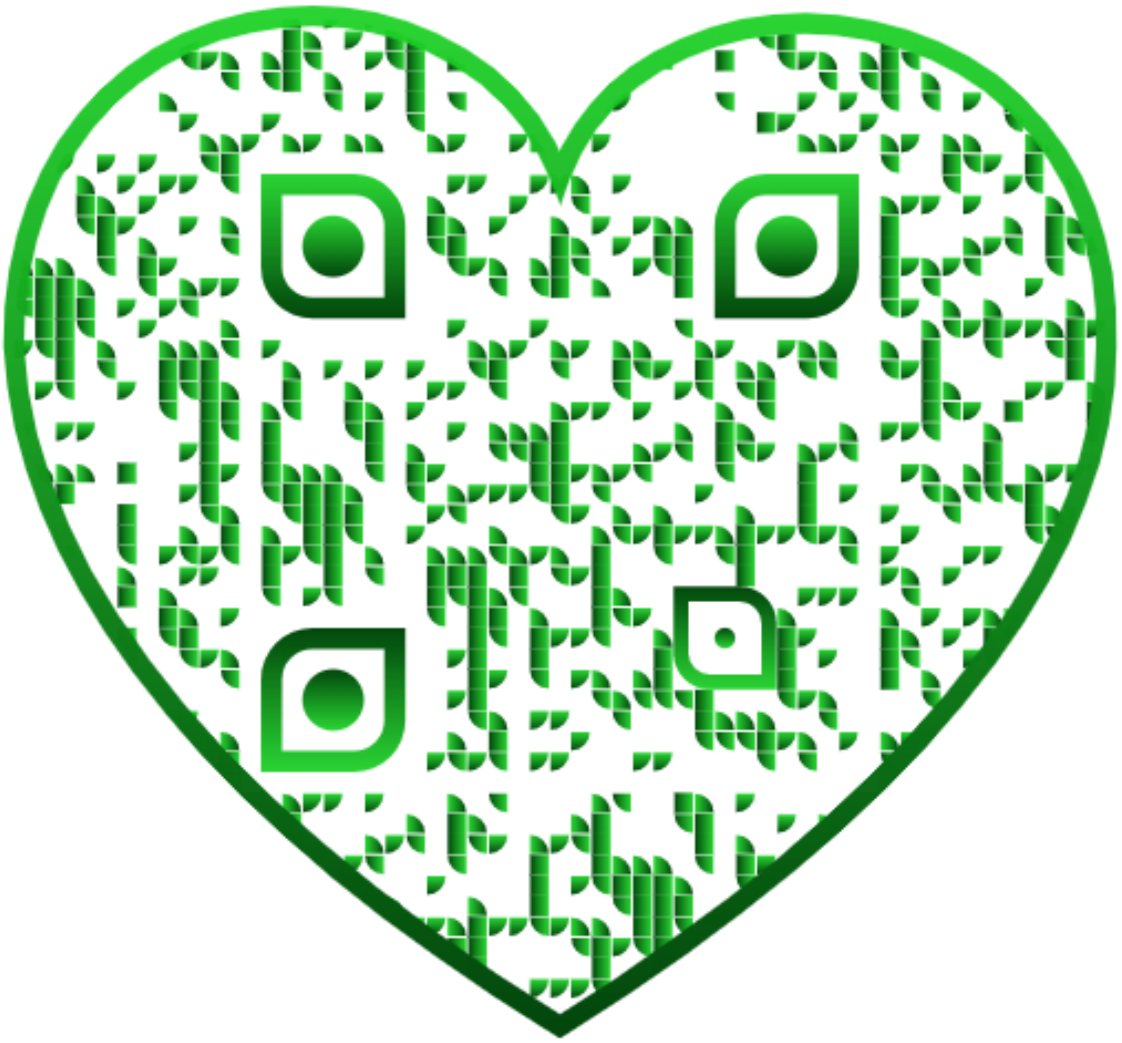
Radiochemical methods



Objectives:

At the end of this cession the students able to

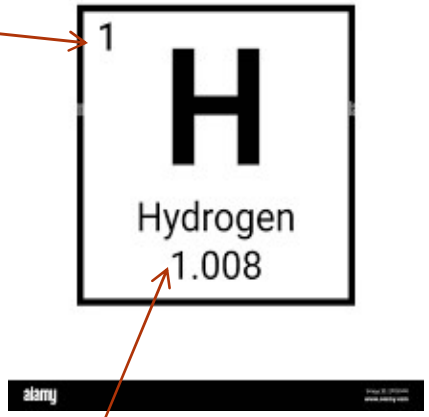
- define non radioactive and radioactive isotopes
- identify the different types of radiations
- explain radioactive decay activity
- determine the unknown mass of sample using different radiochemical methods

Brain storming Questions

What are isotopes?

What is radioactive?

?



Protium
Deuterium
Tritium

?

Introduction

- Radioactive isotopes:
  - have unstable nuclei that spontaneously change to form more stable nuclei.
  - Can emit radiation & / or particles
    - alpha, beta, and gamma rays

- Element when the N/P ratio becomes higher, the nucleus become unstable;
  - Results in the disintegration of the nucleus so as to achieve a stable N/P ratio and therefore a stable nucleus.
    - This process is called radioactive decay.

- **Natural radioactive** - radioactive process can be spontaneous in some naturally occurring nuclides;

- **Artificial radioactive** - instability is brought about by bombarding stable nuclides with high-energy particles.
  - The unstable nuclides disintegrate to form stable nuclides with release of energy and nuclear particles:

Type of radiation

- The most important types of radioactive particles are
  - alpha (α) particles,
  - beta (β) particles,
  - gamma rays (γ) and
  - X-ray.

1. Alpha (α) particle

- are doubly charged, highly energetic helium nucleus
- It consists of 2 proton & 2 neutron (a stream of positively charged helium ions , He^{2+})

$$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He + Energy$$

- Has low penetration power but has high ionization power, they lose energy very rapidly
- can cause extensive damage to organs and tissues
- Not used for treatment & sterilization.

2. Beta (β) particle:

- is a stream of electrons formed as neutrons changed to protons or vice-versa
- β - Particle emission has two forms:
  - Positron (β+) – if it is positive charge $\longrightarrow {}^{65}_{30}Zn \rightarrow {}^{65}_{29}Cu + \beta^{+} + \nu$
  - Negatron (β-) –if it is negative charge $\longrightarrow {}^{14}_{6}C \rightarrow {}^{14}_{7}N + \beta^{-} + \bar{\nu}$
- Have high penetration power
- Used extensively in nuclear medicine for diagnostic and therapeutic applications.

3. Gamma -Rays (γ)

- Gamma rays are produced by nuclear relaxations.
  - The release of energy while the excited nucleus returns to the ground state appears as electromagnetic radiation colled γ ray.
  - Because γ -Emission is EMR, there is no change in the neutron number or mass number or atomic number.
- Has high penetration power & high energy EMR
- Used for sterilization

4. X-ray

- X-Rays originate from orbital electron,
  - Where as γ -Rays originate from the decay of a nuclide.
- X-Ray emission is formed from electronic transitions in which outer electrons fill the vacancies created by the nuclear process.
  - Outer-shell electrons jump to fill the inner-shell vacancy resulting in an electron orbit reshuffling.
  - This process result in the release of X-Rays

Radioactive decay

- Rate of radioactive Decay
  - It is the rate of disintegration of radioactive particles
  - Governed by first order reaction

$$A = dN/dt = \lambda N$$

$$N = N_o e^{-\lambda t} \longrightarrow \log N = \log No - \lambda t/2.303$$

$$A = \lambda N_o e^{-\lambda t} = A_o e^{-\lambda t}$$

  - Where: A = activity (dps)

N = No of radioactive atom present in the sample at time, t

λ = radioactive decay constant

- By measuring the activity at time *t*,
  - *we can determine the initial activity, A0, or the number of radioactive atoms originally present in the sample, N0*
- An important characteristic property of a radioactive isotope is its **half-life,**
  - The time required for half of the initial number of a radioactive isotope's atoms to disintegrate (*t1/2*)
- For first-order kinetics the half-life is independent of concentration and is given as
  - **$t_{1/2} = 0.693/\lambda$**

Application of radioactive isotope

- Radio isotopes are extensively used in:

I. Medicine

- for diagnosis:
  - The radiopharmaceuticals accumulated in an organ of interest emit radiations which are used for imaging of the organs.
- for therapeutic – eg. treatment of cancer
  - Are radio labeled molecules designed to deliver therapeutic doses of ionizing radiation to specific diseased sites.
    - ✓ posses the ability to destroy diseased tissues.
- Sterilization

II. Analytical application - For drug analysis

Quantitative Applications

- Radiochemical methods of analysis:
  - are considerably more sensitive than other chemical methods.
    - it is possible to attain quantitation levels lower than ppb levels of elements.
  - In most cases, can be done without separation of the analyte.
  - **Radiochemical methods of analysis include**:
    - Direct Analysis of Radioactive Analytes
    - Tracer methods - Isotope dilution
    - Neutron activation analysis
    - Radioimmunoassay techniques

1. Direct Analysis of Radioactive Analytes

The sample's activity can be used to calculate the number of radioactive particles that are present in the sample.

Example:

The activity in a 10.00-mL sample of radioactive wastewater containing $^{90}_{38}Sr$ was found to be 9.07×10^6 disintegrations/s. What is the molar concentration of $^{90}_{38}Sr$ in the sample? The half-life for $^{90}_{38}Sr$ is 28.1 years.

Solution:

$A = dN/dt = \lambda N$

$$\lambda = \frac{0.693}{t_{1/2}}$$

$$\frac{(9.07 \times 10^6 \text{ disintegrations/s})(8.86 \times 10^8 \text{ s})}{0.693} = 1.16 \times 10^{16} \text{ atoms of } ^{90}_{38}Sr$$

Thus, the concentration of $^{90}_{38}Sr$ in the sample is

$$\frac{1.16 \times 10^{16} \text{ atoms}}{(6.022 \times 10^{23} \text{ atoms/mol})(0.01000 \text{ L})} = 1.93 \times 10^{-6} \text{ M } ^{90}_{38}Sr$$

2. Tracers Methods of Analysis

- Radioactivity is introduced into the sample by adding a measured amount of a radioactive species.

- A measurement of the redistribution of tracer within such a sample-reagent reaction system provides the required quantitative analytical information

❖ Isotope Dilution

- In isotope dilution analysis;
  - ➢ a known amount of radiolabeled compound (W_T) with known specific activity (A_T) is added to a sample of an unknown mass (W_X) of a non radioactive analyte, & mixed thoroughly.
  - ➢ The sample is then processed to isolate, w_A , grams of purified analyte, containing both radioactive and nonradioactive materials. The activity of the isolated sample, A_A, is measured.
  - ➢ From the specific activities of the tracer before and after dilution, the concentration of the component in the mixture can then be calculated.

$$A_A = A_T\left(\frac{w_A}{w_x + w_T}\right)$$

- The following equation relates the activity of the isolated and purified mixture of analyte and tracer to the original amount of the analyte,

$$w_x = \frac{A_T}{A_A} w_A - w_T$$

- where,

W_T = the grams of tracer having a counting rate of A_T (cpm),

W_A = the grams of isolated sample consisting of active and inactive species with a counting rate of A_A,

W_X= the weight of analyte

Example:

Q.1. The concentration of insulin in a production vat is determined by the method of isotope dilution. A 1.00-mg sample of insulin labeled with ^{14}C, with an activity of 549 cpm, is added to a 10.0-mL sample taken from the production vat. After homogenizing the sample, a portion of the insulin is separated and purified, yielding 18.3 mg of pure insulin. The activity for the isolated insulin is measured at 148 cpm. How many milligrams of insulin are in the original sample?

Solution:

$$w_x = \frac{549 \text{ cpm}}{148 \text{ cpm}} \times 18.3 \text{ mg} - 1.00 \text{ mg} = 66.9 \text{ mg insulin}$$

- Q. 2. The vitamin B_{12} content of a multivitamin tablet is determined by dissolving ten tablets in water. The dissolved tablets are transferred to a 100-mL volumetric flask and diluted to volume. A 50.00-mL portion is removed and treated with 0.500 mg of radioactive vitamin B_{12} having an activity of 572 cpm. After homogenization, the vitamin B_{12} in the sample is isolated and purified, producing 18.6 mg with an activity of 361 cpm. Calculate the average concentration of vitamin B_{12} in the tablet (in milligrams per tablet).

3. Neutron Activation Analysis

- A means of inducing radioactivity in a nonradioactive sample by bombarding the sample with neutrons.
- The radioactive element formed by neutron activation decays to a stable isotope by emitting gamma rays, or other nuclear particles.
- The rate of gamma-ray emission is proportional to the analyte's initial concentration in the sample.

- For example, when a sample containing nonradioactive $^{27}_{13}Al$ is placed in a nuclear reactor and irradiated with neutrons, the following nuclear reaction results.

$$^{27}_{13}\mathrm{Al} + {}^{1}_{0}n \rightarrow {}^{28}_{13}\mathrm{Al}$$

- When irradiation is complete, the sample is removed from the nuclear reactor, allowed to cool and the rate of gamma-ray emission is measured.

$$^{28}_{13}\mathrm{Al} \rightarrow {}^{28}_{14}\mathrm{Si} + {}^{0}_{-1}\beta + \gamma$$

- A simpler approach for analyzing neutron activation data is to use one or more external standards

- Letting *(A0)x and (A0)s represent the initial activity for the analyte* in an unknown and a single external standard, and letting ***wx*** *and* ***ws*** *represent* the weight of analyte in the unknown and the external standard, gives a pair of equations

$$(A_0)_x = kw_x$$

$$(A_0)_s = kw_s$$

- If the samples and standards are irradiated simultaneously, and the activities are measured at the same time, then these activities may be used in place of *(A0)x and (A0)s in the preceding equations*

$$w_x = \frac{A_x}{A_s} \times w_s$$

- Example:

The concentration of Mn in steel can be determined by a neutron activation analysis using the method of external standards. A 1.000-g sample of an unknown steel sample and a 0.950-g sample of a standard steel known to contain 0.463% w/w Mn, are irradiated with neutrons in a nuclear reactor for 10 h. After a 40-min "cooling" period, the activities for gamma-ray emission were found to be 2542 cpm (counts per minute) for the unknown and 1984 cpm for the standard.

What is the **%w/w** Mn in the unknown steel sample?

Solution:

$$w_x = \frac{A_x}{A_s} \times w_s$$

- The weight of Mn in the standard sample is:

$$w_s = \frac{0.00463 \text{ g Mn}}{\text{g steel}} \times 0.950 \text{ g steel} = 0.00440 \text{ g Mn}$$

$$w_x = \frac{2542 \text{ cpm}}{1984 \text{ cpm}} \times 0.00440 \text{ g Mn} = 0.00564 \text{ g Mn}$$

- % w/w Mn = 0.00564g mn/ 1 g steel x 100 = 0.564 % Mn

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